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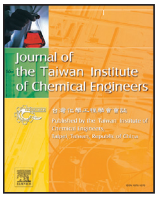

Plasma-assisted fabrication of nanoparticle-decorated electrospun nanofibers

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ABSTRACT

Recent developments of functional nanoparticle-decorated electrospun nanofibers have attracted much attention. In this work, plasma treatment was introduced as a simple, efficient, green and versatile method for the fabrication of nanoparticle-decorated electrospun nanofibers. The size of the formed nanoparticles on the nanofibers could be readily tuned by controlling the plasma etching time. Moreover, various nanoparticles could be generated on the nanofibers by mixing different metal salts in the precursor nanofibers. The nanoparticle-decorated nanofibers showed promising surface enhanced Raman scattering properties, and allowed the detection of rhodamine 6 G molecules at concentrations as low as 10^{-12} M.

1. Introduction

Polymer/nanoparticle hybrid organic/inorganic materials have drawn extensive interest in recent years because of their fascinating properties and applications [1,2]. One dimensional polymer electrospun nanofibers have been considered as classic templates for the decoration of various kinds of nanoparticles (NPs), benefiting from the fast development of the simple, cost-efficient and versatile electrospinning technique [3–5].

Generally speaking, NPs-decorated electrospun nanofibers could be fabricated by both ex-situ and in-situ methods, such as mixing NPs in the electrospinning solution, nanofiber-templated assembly of NPs, in-situ reduction, gas–solid reaction and calcination [6,7]. Since the delicate synthesis of NPs is required for the ex-situ methods, the in-situ methods are more straightforward. For example, Wang group has developed a facile approach for the fabrication of NPs-doped electrospun nanofibers through gas–solid reaction [8]. NPs such as PbS, Ag_2S and AgCl NPs could be formed on the nanofibers by exposing the precursor nanofibers to H_2S or HCl gas [8–10]. In other examples, the in-situ reduction strategy is widely used due to its simplicity. The metal salts on the precursor nanofibers could be reduced to metal NPs via thermal reduction, photoreduction or chemical reduction [11–14]. Song and co-workers reported that ultrafine Au NPs could be anchored on the hierarchical double-walled nickel silicate hollow electrospun nanofibers using an in situ reduction method [15]. The hybrid material showed high catalytic activity and excellent stability during the catalytic reduction of 4-nitrophenol. Recently, Jiang and co-workers reported that oxygen plasma etching of the pristine electrospun nanofibers could facilitate the seeding and growth of Ag NPs on the nanofibers via a multistep process [16]. The key for the successful fabrication is the increased hydrophilicity by using the plasma treatment. Although all these methods have been proved to be efficient tools for the fabrication of functional NPs-decorated nanofibers, there are some shortcomings, including time-consuming process, multistep operations and hazardous preparation, which might limit their further development and application. Therefore, a simple, efficient, green and versatile method is urgently needed for the fabrication of NPs-decorated electrospun nanofibers.

Here, plasma treatment was used to directly generate various NPs on the electrospun nanofibers. The metal salts in the precursor nanofibers could be directly reduced into metal NPs during the plasma treatment. The size of the decorated NPs could be conveniently tuned by controlling the plasma etching time. Moreover, the NPs-decorated electrospun nanofibers showed promising surface enhanced Raman scattering (SERS) properties, which might be applied in the sensing field.

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2. Experimental section

2.1. Materials

Silver nitrate ($AgNO_3$, 99.8%), chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$, AR), *N,N*-dimethylmethanamide (DMF, AR) and tetrahydrofuran (THF, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyacrylonitrile (PAN, $M_w = 85{,}000$ g/mol) was purchased from Shanghai Jinshan Chemical Co., Ltd. 4-aminothiophenol (4-ATP) and rhodamine 6 G (R6G) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Preparation of Ag NPs decorated electrospun nanofibers

The PAN/$AgNO_3$ precursor solution was prepared by dissolving 0.15 g $AgNO_3$ powder in 3 g 10 wt% PAN/DMF solution under stirring in the dark for 24 h. Then, the PAN/$AgNO_3$ nanofibers were electrospun from the precursor solution. The precursor solution was placed into a 10 mL of syringe with a stainless steel needle (inner diameter: 0.7 mm) and pumped continuously at a rate of 500 µL/h. The applied voltage was fixed at 15 kV. The collection distance was 15 cm. After electrospinning for 1 h, the electrospun nanofibers formed into a piece of white membrane on the grounded aluminum foil. Subsequently, the obtained PAN/$AgNO_3$ nanofibers were treated with argon plasma (50 W, 100 mTorr, 10 sccm, PE-25 plasma system, Plasma Etch, Inc. USA) for different time periods. Finally, the Ag NPs decorated PAN nanofibers were obtained.

2.3. Preparation of Au NPs decorated electrospun nanofibers

The Au NPs decorated electrospun nanofibers were fabricated similarly. The PAN/$HAuCl_4$ precursor solution was prepared by mixing 0.33 g 10 wt% $HAuCl_4$/THF solution with 1 g 11 wt% PAN/DMF solution under vigorous stirring for 1 h. Then, the PAN/$HAuCl_4$ nanofibers were electrospun from the precursor solution. The precursor solution was placed into a 10 mL of syringe with a stainless steel needle (inner diameter: 0.7 mm) and pumped continuously at a rate of 300 µL/h. The applied voltage was fixed at 15 kV. The collection distance was 15 cm. After electrospinning for 1 h, the obtained PAN/$HAuCl_4$ nanofibers were treated with air plasma (50 W, 100 mTorr, 10 sccm) for 3 min. Finally, the Au NPs decorated PAN nanofibers were obtained.

2.4. Characterization

The morphologies of the PAN/$AgNO_3$ and PAN/$HAuCl_4$ nanofibers before and after the plasma treatment were observed by a field emission scanning electron microscopy (SEM, Hitachi SU-8010). In order to clearly observe the generated NPs, the obtained PAN/Ag and PAN/Au nanofibers were not sputtered with gold. The size distribution of the NPs on the nanofiber was analyzed using Nano Measure free software. The morphologies of the PAN/$AgNO_3$ nanofibers before and after the plasma treatment were obtained by a transmission electron microscopy (TEM, JEOL-2100F). The X-ray diffraction (XRD) analysis was carried out on a DX-2700 X-ray diffractometer with a Cu Kα radiation source ($\lambda = 0.154$ nm).

The SERS properties of the NPs decorated nanofibers were investigated using both 4-ATP and R6G as probing molecules. The as-prepared nanofiber membranes (1 cm × 1 cm, including the PAN/$AgNO_3$ membrane, the PAN/Ag membrane, the PAN/Au membrane, etc.) were immersed into 1 mL of the analyte solution with different concentrations for 6 h. After drying in the air for several hours, SERS measurements were conducted on the substrates. A Renishaw InVia confocal Raman spectrometer operating at 532 nm (50 mW) and 785 nm (300 mW) was used to analyze the SERS performance. The excitation power was 0.025 mW (0.05% of the maximum power, 532 nm) and 3 mW (1% of the maximum power, 785 nm) for the Ag NPs and Au NPs decorated nanofibers, respectively. The integral time was 10 s.

3. Results and discussion

It is known that energetic species such as ions, electrons, free radicals and neutrals are generated during the plasma treatment [17,18]. These activated species can interact with materials through physical bombardment and chemical reactions [19]. The idea of this work is to obtain one dimensional NPs-decorated electrospun nanofiber by simultaneous etching of the polymer part of the precursor nanofiber and reducing the exposed metal salts into NPs. As shown in Fig. 1a, the PAN/$AgNO_3$ precursor nanofibers with a diameter of about 180 nm were rather smooth. After the argon plasma treatment (50 W, 3 min), the color of the nanofiber membrane turned from white to deep brown (Fig. S1 in the Supporting Information), and NPs with diameter of about 18.04 nm were clearly observed on the nanofibers (Fig. 1b). The metal salts from the PAN/$AgNO_3$ precursor nanofibers were reacted with the electrons in the plasma, and reduced to crystalline metal NPs [20,21]. The emergence of the NPs on the electrospun nanofibers proves that this short and green plasma treatment is effective to generate NPs from the precursor nanofiber.

In order to obtain a better insight into the formed NPs on the nanofibers, TEM observations as well as XRD experiments were conducted on the nanofibers before and after the argon plasma treatment. The TEM image shown in Fig. 2a displays the PAN/$AgNO_3$ precursor nanofiber. The small dark dots on the nanofiber might result from the electron irradiation during the TEM observation or the slight reduction of Ag^+ by the DMF solvent. Notably, NPs with relatively uniform size were obtained on the plasma-treated nanofiber (Fig. 2b), which was consistent with the SEM results (Fig. 1b). The high resolution TEM image (Fig. 2c) further suggests that Ag NPs are generated on the nanofiber (namely PAN/Ag nanofiber), since the lattice fringes with a spacing of 0.24 nm represent the (111) planes of face-centered cubic silver [20,21]. Further evidence of the formation of Ag NPs was also shown in the XRD patterns (Fig. 2d). After the plasma treatment, new peaks located at 38.4°, 44.1° and 64.5°, which could be assigned to Ag (111), (200) and (220) planes, were found in the XRD pattern [20]. This also confirms that the decorated NPs are Ag NPs. The strong diffraction peak centered at 17.1° and the weak diffraction peak centered at 28.4° represented the X-ray reflections of the (100) and (110) crystallographic planes in PAN [22]. The crystallization of the PAN molecules might be promoted by the heat generated in the plasma. It is worth noting that no obvious content of silver oxides was detected for the as-prepared PAN/Ag electrospun nanofibers, which might arise from the usage of argon plasma. The peak located at 31.6°, which could be ascribed to silver oxides, was found after the PAN/Ag nanofiber membrane was stored for 45 days.

A predominant advantage of the plasma treatment is that the process is controllable. Thus, the size of the NPs could be readily tailored by varying the plasma etching time (Fig. 3 and Fig. S7). The sizes of the generated Ag NPs were about 10.69 nm, 11.60 nm, 18.04 nm and 17.62 nm for the PAN/Ag nanofibers after 1 min, 2 min, 3 min and 4 min plasma treatment, respectively. Clearly, the size of the generated Ag NPs increased with the increasing plasma etching time, since more silver salts were exposed and reduced after a longer plasma treatment. However, the size of the formed NPs did not further increase after 4 min plasma treatment, and the density of the formed NPs seemed to increase slightly. What is more, it should be noted that the nanofiber membrane might be

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